

Lithium-mediated Ferration of Fluoroarenes

Lewis C. H. Maddock^a, Alan Kennedy^b, and Eva Hevia^{*a}

Abstract: While fluoroaryl fragments are ubiquitous in many pharmaceuticals, the deprotonation of fluoroarenes using organolithium bases constitutes an important challenge in polar organometallic chemistry. This has been widely attributed to the low stability of the *in situ* generated aryl lithium intermediates that even at $-78\text{ }^{\circ}\text{C}$ can undergo unwanted side reactions. Herein, pairing lithium amide LiHMDS (HMDS = $\text{N}(\text{SiMe}_3)_2$) with $\text{Fe}^{\text{II}}(\text{HMDS})_2$ enables the selective deprotonation at room temperature of pentafluorobenzene and 1,3,5-trifluorobenzene *via* the mixed-metal base $[(\text{dioxane})\text{LiFe}(\text{HMDS})_3]$ (**1**) (dioxane = 1,4-dioxane). Structural elucidation of the organometallic intermediates $[(\text{dioxane})\text{Li}(\text{HMDS})_2\text{Fe}(\text{Ar}^{\text{F}})]$ (Ar^{F} = C_6F_5 , **2**; 1,3,5- $\text{F}_3\text{-C}_6\text{H}_2$, **3**) prior electrophilic interception demonstrates that these deprotonations are actually ferrations, with Fe occupying the position previously filled by a hydrogen atom. Notwithstanding, the presence of lithium is essential for the reactions to take place as $\text{Fe}^{\text{II}}(\text{HMDS})_2$ on its own is completely inert towards the metallation of these substrates. Interestingly **2** and **3** are thermally stable and they do not undergo benzyne formation *via* LiF elimination.

Keywords: Cooperative bimetallics · Deprotonative metallation · Fluoroarenes · Iron · Lithium



Lewis C. H. Maddock obtained his MSci in Pure and Applied Chemistry from the University of Strathclyde (UK), completing his final year project with Prof. Rab Mulvey. From 2012–2016 he carried out his PhD research on alkali-metal ferrate complexes at the same institution working with Prof. Eva Hevia. After two years of postdoctoral work concerning Single-Molecule Magnet ligand strategies with Prof. Richard Layfield at the

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1. Introduction

Amongst the different tools available for the functionalisation of aromatic molecules, *Directed ortho-Metallation (DoM)* is arguably one of the most powerful and widely used in synthesis.^[1–4] Polar organometallics such as lithium amide LiTMP (TMP = 2,2,6,6-tetramethylpiperidine) or organolithiums RLi are usually the reagents of choice,^[5–7] although in many cases their applications can be compromised by their moderate selectivity and limited functional group tolerance.^[8] This is particularly challenging for the deprotonation of fluoroarenes. While highly electronegative, fluorine is a good *ortho* directing group, increasing the acidity of its neighbouring H atoms. The main limitation is the lack of stability of the metallated intermediates generated (*e.g.* benzyne formation, autometallation and cascade processes),^[9] as illustrated by Schlosser in a seminal study on the deprotonation of 1,3,5-trifluorobenzene by BuLi .^[10] To address some of these challenges and considering the prominent role of fluoroarenes in pharmaceutical synthesis, where around 20–25% of forthcoming drugs contain at least one F atom,^[11,12] several alternative *s*-block organometallic strategies have been developed using single-metal bases but also mixed-metal reagents. This includes the use of

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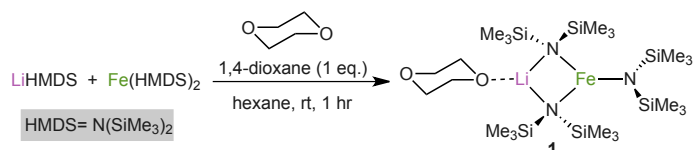
lithium zincates developed by Uchiyama^[13] which generate more stable arylzinc intermediates, that can be subsequently quenched, enabling the metallations to take place at room temperature. Magnesium of fluoroarenes has also been accomplished under mild reaction conditions employing magnesium bases supported by the bulky β -diketiminato ligand which provides steric protection to the highly reactive fluoroaryls.^[14] *s*-Block metals can also work in tandem with main-group metals, as shown for the deprotonation of fluoroarenes using LiTMP in combination with $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (via trans-metal-trapping (TMT) approaches),^[15,16] where the lithium amide metalates the substrate while the gallium alkyl traps and stabilises the sensitive carbanion, which can subsequently be employed in Pd-catalysed C–C bond forming processes.^[17] Along with these main-group-metal-mediated strategies, Knochel has used the trimetallic combination $(\text{TMP})_2\text{Fe} \cdot 2\text{MgCl}_2 \cdot 4\text{LiCl}$ for the functionalisation of a range of fluoroarenes via deprotonative metallation followed by Ni-catalysed cross-coupling with alkyl halides.^[18] In this study *ortho*-ferration of the aromatic substrates was proposed, although the constitutions of the organometallic intermediates involved remained undetermined.

Inspired by these studies, we have recently investigated the metallating ability of iron(II) *bis*(amide) $\text{Fe}^{\text{II}}(\text{HMDS})_2$ ($\text{HMDS} = \text{N}(\text{SiMe}_3)_2$),^[19] which is isostructural in the solid state with the parent $\text{Mg}(\text{HMDS})_2$.^[20] Interestingly, while on its own this compound fails to deprotonate fluoroarenes, when partnered with group 1 amide NaHMDS and forming sodium ferrate $[(\text{dioxane})_{0.5}\text{NaFe}(\text{HMDS})_3]$, we can perform regioselective direct ferration of a variety of fluoroarenes under mild conditions, a rare example where Fe can perform a metallation reaction.^[21] These studies hinted at a crucial effect of the alkali metal, acting as a facilitator that ultimately leads to the direct Fe–H exchange process, which appears to be directed by the initial coordination of the substrate to sodium. Thus, these reactions can be described as *alkali-metal-mediated ferrations* (AMMFe).^[15] Extending the scope of this approach to other *s*-block metals, here we investigate the synthesis of a heterobimetallic lithium-iron base and assess its reactivity towards fluoroarene metallation.

2. Results and Discussion

2.1 Synthesis of Mixed-Metal Amide Base 1

Akin with our reported studies on sodium ferrates,^[21,22] we began with the monometallic HMDS compounds LiHMDS and $\text{Fe}(\text{HMDS})_2$, which were combined in hexane, quickly forming a homogeneous light green solution at ambient temperature (Scheme 1). To this mixture, 1 eq. of 1,4-dioxane was added resulting in the precipitation of a pale green solid which could be crystallised after solubilising in fluorobenzene and cooling to -30°C . X-ray crystallographic analysis revealed the structure of $[(\text{dioxane})\text{LiFe}(\text{HMDS})_3]$ (**1**) which could be recovered in a 70% yield (Fig. 1).



Scheme 1. Synthesis of lithium ferrate base **1**.

Heterobimetallic **1** exhibits a discreet contacted-ion pair structure, where Li and Fe are connected by two bridging HMDS amido groups with a further terminal HMDS residing on Fe. Unsurprisingly the Fe–N bond distances for the bridging amido groups are slightly elongated when compared to that of terminal

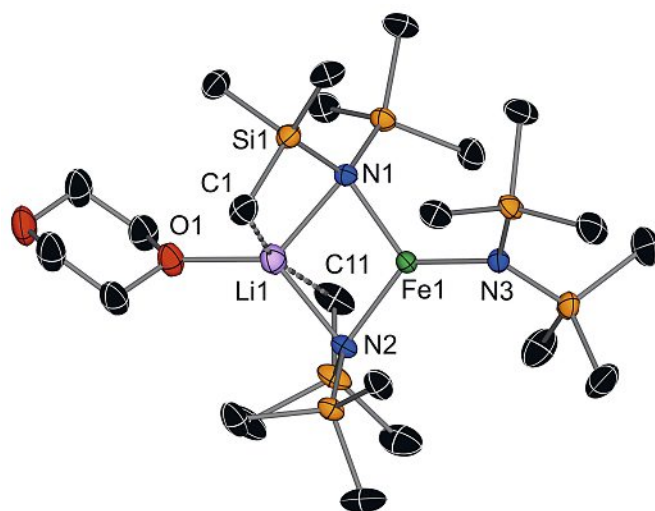


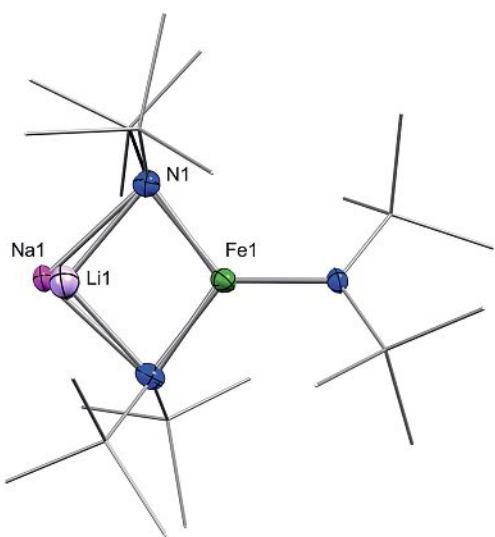
Fig. 1. Molecular structure of $[(\text{dioxane})\text{LiFe}(\text{HMDS})_3]$ (**1**). Hydrogen atoms omitted for clarity. Thermal ellipsoids displayed at 50% probability level.

HMDS [mean value 2.0511 vs 1.9604(19) Å]. Lithium completes its coordination sphere binding to a terminally coordinated molecule of 1,4-dioxane [$\text{Li1} \cdots \text{O1}$ 1.991(5) Å] as well as forming two long-distance interaction with two methyl groups, each of them belonging to a different bridging HMDS ligand [$\text{Li} \cdots \text{C1}$, 2.785(5) and $\text{Li} \cdots \text{C11}$, 2.829(5) Å, shown as dashed bonds in Fig. 1]. Interestingly a comparison of the geometrical parameters of **1** with those previously reported by Layfield for its unsolvated congener $[\text{LiFe}(\text{HMDS})_3]$,^[23] showed that while the coordination environment around Fe in both compounds is almost identical, the Li–N bonds [mean values, 2.041 vs 2.134 Å in **1**] and $\text{Li} \cdots \text{Me}$ electrostatic interactions [mean value 2.332 Å] are noticeably shorter for the latter. A similar trend was noted for the sodium analogue of **1**, $[(\text{dioxane})_{0.5}\text{NaFe}(\text{HMDS})_3]$,^[21] with almost identical Fe–N bond distances to those witnessed in **1** but significantly elongated Na–N distances [mean value, 2.464 Å], consistent with the larger size of Na (see Table 1 for details). No $\text{Na} \cdots \text{C}$ long distance interactions were observed for this complex which exhibits a dimeric structure, with dioxane bridging two $\{\text{NaFe}(\text{HMDS})_3\}$ fragments.^[21] These bonding preferences ultimately translate to the Li atom being ‘sunk’ further into the steric sphere of the $\{\text{Fe}(\text{HMDS})_3\}^-$ unit, in closer proximity to Fe at a distance of 2.665(4) Å (vs $\text{Na1} \cdots \text{Fe1}$ 2.9995(6) Å in the sodium ferrate complex, see Fig. 2 and Table 1). These structural features can be rationalised considering the anchoring/ancillary bonding model previously described by Mulvey for *s*-block heterobimetallic chemistry.^[24] Thus, the shorter and more covalent Fe–N interactions can be described as anchoring bonds, providing the $\{\text{Fe}(\text{HMDS})_3\}^-$ foundation units for these structures, to which the alkali metals (AM) are affixed by a combination of weaker AM–N and $\text{Li} \cdots \text{CH}_3$ ancillary bonds.

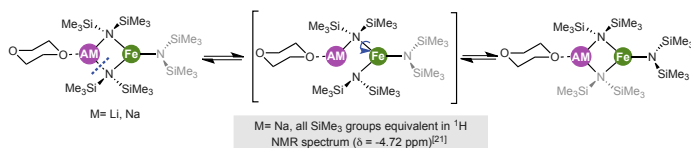
The solution-phase effective magnetic moment of **1** ($5.36 \mu_B$) was determined using Evans method,^[26–28] which is in the range of the spin-only magnetic moment value ($4.90 \mu_B$) for a high-spin ($S = 2$) Fe(II) centre. The paramagnetic ^1H NMR spectrum of **1** in d_8 -toluene solutions displays three very broad resonances centred at 21.06, 10.21 and -2.46 ppm. While the paramagnetic shifting and extensive broadening of these signals makes their assignment particularly challenging,^[29] a comparison of this spectrum with that recorded for $[\text{LiFe}(\text{HMDS})_3]$ (see Supporting Information) allows the assignment of the signal of 21.06 to the coordinated molecule of dioxane, whereas the resonances at 10.21 and -2.46 ppm are tentatively assigned to the terminal and bridging HMDS groups, respectively. This differentiation between terminal and bridging amide ligands is also present in $[\text{LiFe}(\text{HMDS})_3]$ (8.80 and -2.20 ppm respectively, see Supporting Information) but contrasts

Table 1. Selected bond distances (Å) and angles (°) for complexes **1–3** (AM = Li) and [(dioxane)_{0.5}NaFe(HMDS)₃].^[21]

	1	2	3	[(dioxane) _{0.5} NaFe(HMDS) ₃]
Fe1–N1	2.0474(19)	1.990(4)	2.007(3)	2.0378(12)
Fe1–N2	2.0548(18)	2.009(3)	2.017(3)	2.0625(11)
Fe1–N3	1.9604(19)	–	–	1.9443(12)
Fe1–C13	–	2.092(4)	2.078(4)	–
AM1–N1	2.133(5)	2.098(8)	2.080(8)	2.4395(13)
AM1–N2	2.135(5)	2.141(9)	2.135(8)	2.4894(13)
AM1–O1	1.991(5)	1.954(9)	1.943(8)	2.2828(12)
Fe1---AM1	2.665(4)	2.649(8)	2.661(7)	2.9995(6)
N1–Fe1–N2	103.41(8)	103.96(14)	102.72(13)	109.17(5)
N1–Fe1–N3	125.99(8)	–	–	125.93(5)
N2–Fe1–N3	130.39(8)	–	–	124.91(5)
N1–Fe1–C13	–	126.99(16)	127.70(15)	–
N2–Fe1–C13	–	129.05(16)	129.57(14)	–
N1–AM1–N2	97.93(18)	96.0(3)	96.4(3)	85.36(4)

Fig. 2. Overlay of {MFe(HMDS)₃} structures of **1** and [(dioxane)_{0.5}NaFe(HMDS)₃].^[21] Overlay of N1, Fe1 and N2 atoms in Mercury.^[25] SiMe₃ units depicted as wires and a terminal HMDS group, solvating 1,4-dioxane groups and hydrogen atoms omitted for clarity.

with previous ¹H NMR spectra reported for related sodium ferrates where just a single broad signal is observed for the HMDS groups (Scheme 2).^[21,22] These spectroscopic findings correlate with the structural studies showing that Li is noticeably more embedded within the coordination pocket created by the {Fe(HMDS)₃}[–] anion than Na (Fig. 2). Assuming that the interconversion between bridging/terminal HMDS groups in these ferrates takes places *via* the initial cleavage of one AM–N_{bridging} bond (AM = alkali metal), followed by rotation around the remaining Fe–N_{bridging} bond and formation of a new AM–N bond to close a four-membered {AMNFeN} ring (as depicted in Scheme 2), it should be expected for this fluxional process to be faster for Na than for Li. Accordingly, at room temperature all HMDS groups appear equivalent in the ¹H NMR spectrum for the sodium ferrate but for **1** two distinct signals for the terminal and bridging HMDS groups are observed.

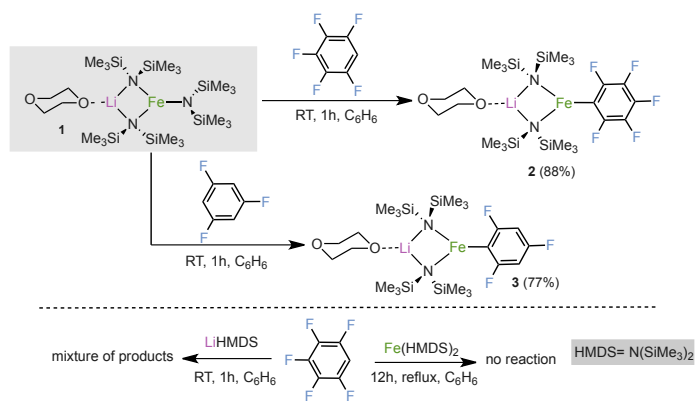
Scheme 2. Proposed fluxional process that interconverts bridging and terminal HMDS groups in alkali-metal ferrates [(dioxane)_xAMFe(HMDS)₃] (AM = Li, x = 1; AM = Na, x = 0.5).

It should also be noted that when the ¹H NMR of **1** is carried out in the coordinating solvent *d*₈-THF, a single signal is observed for the HMDS groups at –2.34 ppm but in this case this is most likely due to the formation of a solvent-separated ion pair {Li(THF)_x}⁺{Fe(HMDS)₃}[–] species. Nevertheless in both deuterated solvents, THF or toluene, the bimetallic constitution of **1** is preserved and no evidence was observed in solution for this lithium ferrate to be in equilibrium with its single-metal components Li(HMDS) and Fe(HMDS)₂.

2.2 Assessing the Metallating Ability of **1** towards Selected Fluoroarenes

The reactivity of heterobimetallic amide **1** was probed using pentafluorobenzene and 1,3,5-trifluorobenzene as model substrates (Scheme 3). Reactions were carried out using benzene as a solvent, and stoichiometric amounts of the relevant fluoroarene. In both cases, they were accompanied by a distinctive colour change from pale green to brown, which occurs almost immediately as the relevant fluoroarene was introduced. Slow cooling of these solutions afforded [(dioxane)Li(HMDS)₂Fe(C₆F₅)] (**2**) and [(dioxane)Li(HMDS)₂Fe(1,3,5-F₃-C₆H₂)] (**3**) in 88% and 77% yields respectively (Scheme 3).

X-ray crystallographic studies established the molecular structures of **2** and **3** and demonstrated that these reactions are formally ferrations in which a strong Fe–C σ-bond is formed [2.092(4) Å, **2**; 2.078(4) Å, **3**]. Interestingly the metallated fluoroaryl binds terminally to iron and does not interact with the lithium centre which displays a similar coordination environment to that previously described for **1** (Figs 3 and 4 and Table 1 for further details). Denoting



Scheme 3. Lithium mediated ferration of pentafluorobenzene and 1,3,5-trifluorobenzene by heterobimetallic *tris*(amide) base **1** to give **2** and **3** respectively.

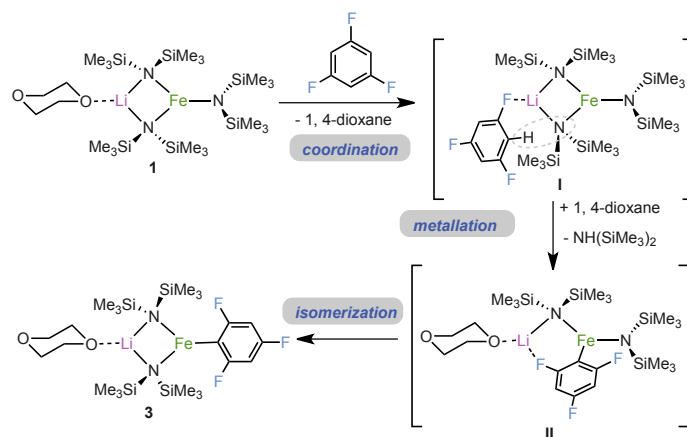
a clear alkali-metal effect, the metal-coordination modes present in **2** and **3** contrast with those reported by us on the metallation of 1,3-difluorobenzene by [(dioxane)_{0.5}NaFe(HMDS)₃], where the fluoroarene adopts a bridging disposition between Na and Fe, with Na forming a dative bond with one of the fluorine atoms. These Na...F interactions have been proposed to direct the regioselectivity of the metallation and provide further stabilisation.

Compounds **2** and **3** were also characterised by ¹H NMR spectroscopy using C₆D₆. The spectrum of **2** shows a very broad resonance centred at −2.69 ppm corresponding to the HMDS groups and a much sharper resonance at 7.64 ppm for the 1,4-dioxane protons. Similarly, for **3**, a very broad resonance centred at −3.70 ppm is visible (HMDS) along with a much sharper signal at 9.79 ppm (1,4-dioxane). Located far downfield, an informative resonance at 105.60 ppm integrating to two protons is also observed, corresponding to the aryl protons. Solution-phase effective magnetic moments of 4.98 and 4.53 μ_B for **2** and **3**, respectively, were determined using Evans method, again corresponding to high-spin (*S* = 2) Fe(II) centres.

Compounds **2** and **3** are stable in solution at room temperature and even at higher temperatures (refluxing in benzene for 6 hours) no decomposition is observed. This thermal stability is in sharp contrast with the marked fragility observed in lithiated fluoroaryls, where, in some cases, even working at −78 °C fast decomposition could be observed.^[10] As shown in Scheme 3, the formation of **2** and **3** is truly synergistic in origin since none of the single components of the heterobimetallic base **1**, LiHMDS or Fe(HMDS)₂ can successfully selectively deprotonate pentafluorobenzene at room temperature on their own. Furthermore, while crystallographic studies establish unequivocally that these

M–H exchange reactions are formal ferrations, the presence of lithium seems to be key to promote these metallations. Thus, these processes can be envisaged as lithium-mediated ferrations for the reactions with 1,3,5-trifluorobenzene, as shown in Scheme 4. As previously proposed for the heterobimetallic sodium-ferrate,^[21] a plausible mechanism may involve initial coordination of the fluoroarene to lithium which fixes the regioselectivity of the reaction (**I** in Scheme 4). This activates the substrate towards deprotonation by one of the bridging amido groups of **1**, furnishing intermediate **II** in which the fluoroaryl is acting as a bridge between the two metals, binding to Fe through its metallated C and to lithium *via* one of its F atoms. Isomerisation of **II** *via* cleavage of the Li...F contact, followed by rotation around the remaining Fe–N bond of the remaining bridging HMDS, enables the switching of the bridging/terminal positions of the aryl and HMDS groups in **II**, furnishing **3**, which is the final product detected and structurally characterised (Fig. 4). This isomerisation step can be driven by the coordination preference of Li which prefers to strongly bond the two HMDS groups rather than just one of them and one of the F atoms of the metallated aryl (**II** in Scheme 4). Interestingly in the case of Na, **II** is the final product of the reaction and no isomerisation step is observed.^[21]

Related to these findings, another interesting alkali-metal effect has been noticed for these reactions. Reacting 1,3,5-trifluorobenzene with two molar equivalents of [(dioxane)_{0.5}NaFe(HMDS)₃] led to the 2,4-diferration of this fluoroarene, affording a thermally unstable intermediate that rapidly eliminates NaF when the temperature is raised to 60 °C.^[21] Contrastingly, even when 1,3,5-trifluorobenzene is reacted with a 2 molar excess of **1**,



Scheme 4. Proposed mechanism for the lithium-mediated ferration of 1,3,5-trifluorobenzene executed by **1**.

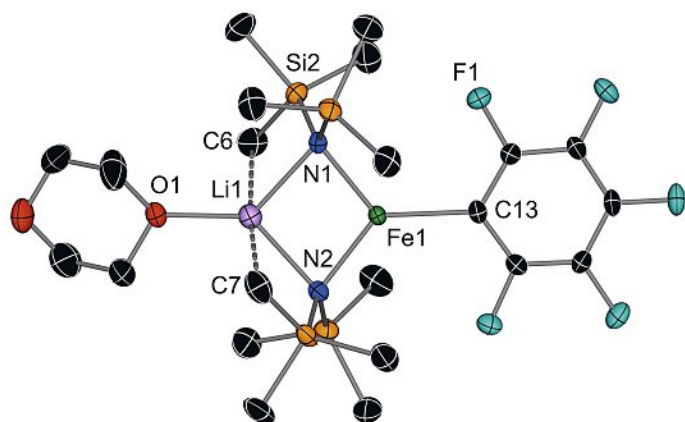


Fig. 3. Molecular structure of [(dioxane)Li(HMDS)₂Fe(C₆F₅)] (**2**). Hydrogen atoms omitted for clarity. Thermal ellipsoids displayed at 50% probability level.

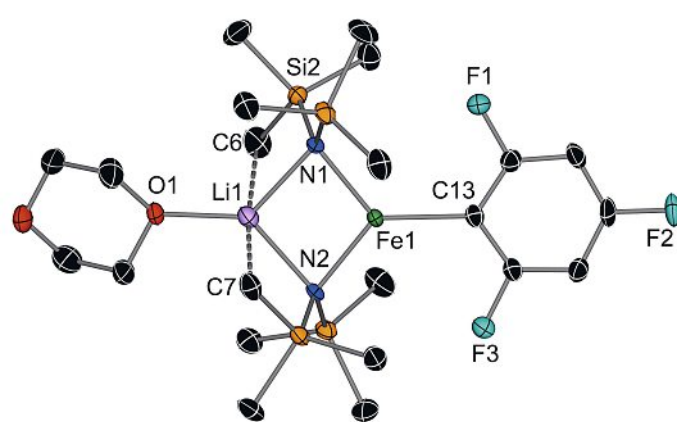


Fig. 4. Molecular structure of [(dioxane)Li(HMDS)₂Fe(1,3,5-F₃-C₆H₂)] (**3**). Hydrogen atoms omitted for clarity. Thermal ellipsoids displayed at 50% probability level.

monoferrated species **3** is the only product obtained in the reaction, which is thermally robust and does not decompose at higher temperatures.

Interestingly many reactions of transition metal complexes with fluoroarenes seem to favour C–F versus C–H bond activation, especially for substrates that have a high degree of fluorination.^[31] In particular, work by Holland has shown that Fe(II) complexes can promote C–F bond activation of perfluoroaromatics, including pentafluorobenzene^[32] and the same reactivity preference has also been noted for Fe(0) species.^[33] Contrastingly here, the cooperative partnership of Li and Fe enables chemoselective transformation of C–H bonds into C–Fe bonds, leaving the C–F sites of the substrates intact. Reactions appear to be driven by the activation of the hydrogens in the fluoroarene substrates in terms of pK_a values (29.0 and 31.5 for C_6F_5H and $C_6F_3H_3$, respectively).^[34] This reactivity pattern is usually associated to main group polar organometallics such as organolithium reagents, however here, the metallation is ultimately delivered by the transition metal, yielding ferration products **2** and **3**.

3. Conclusions

By isolating and structurally defining lithium ferrate **1** and its metallation products **2** and **3**, we report a new bimetallic approach which enables the regioselective functionalisation of fluoroarenes *via* Fe–H exchange reactions. While deprotonation of fluoroarenes using conventional lithium bases can be challenging due to the exceptionally fragility of the generated intermediates, these lithium-mediated ferrations occur regioselectively at room temperature affording thermally stable products. By comparison with previous work using sodium ferrates, insights into the effects of the alkali-metal have been realised which affect both the structure and reactivity of the mixed-metal species involved in these transformations. Collectively these findings open new ground towards designing new synthetic strategies for fluoroarene functionalisation by exploiting the synergic partnership of Li and Fe when both metals are integrated within the same molecular scaffold.

Supplementary Information

Supplementary information is available on <https://www.ingentaconnect.com/content/scs/chimia>

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